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September 13, 2020

Souad Benromdhane, PhD  
Office of Air Quality Planning and Standards Mail Drop C539-07  
U. S. EPA  
109 TW Alexander Drive  
Research Triangle Park, NC 27709

Dear Dr. Benromdhane:

Halocarbon Products Corporation requests the U.S. Environmental Protection Agency (EPA or Agency) to exempt the chemical 1,1,1,3,3,3-hexafluoro-2-methoxypropane (HFMOP or HFE-356mmz1), CAS RN 13171-18-1, from the Agency's definition of the term volatile organic compound (VOC). This exemption would allow HFE-356mmz1 to be used in the U.S. without regulation as a potential precursor to tropospheric ozone under the requirements in 40 CFR 51.100(s). HFE-356mmz1 has very low potential to generate ozone in the troposphere. Its maximum incremental reactivity (MIR) value is estimated to be 0.026 (best estimate) and 0.034 (upper limit) O<sub>3</sub>/gm VOC which is 8x lower than the MIR of ethane on a mass basis (see attached report from Dr. William Carter on the atmospheric reactivity of HFE-356mmz1 and the propensity of this molecule to contribute to tropospheric ozone formation).

**HFE-356mmz1 Background:**

HFE-356mmz1 is a compound of interest to the Halocarbon Products Corporation. Its use and manufacture may result in it being emitted into the atmosphere, where it may be subject to VOC regulations aimed at reducing ozone formation. HFE-356mmz1 will be used as a vapor cleaning solvent with metals, electronics, and precision cleaning. HFE-356mmz1 has been produced in the US for many years as a precursor to the manufacture of Sevoflurane, an anesthetic agent for the induction and maintenance of general anesthesia.

Table 1 includes a summary of available physical-chemical, environmental fate, ecotoxicity, and mammalian toxicity data for HFE-356mmz1. More detailed information can be found in the EU REACH dossier for this substance: <https://echa.europa.eu/registration-dossier/-/registered-dossier/29864/1> and copies of relevant study reports can be provided as necessary.

Halocarbon has established an occupational exposure limit of 790 ppm (ceiling) for this substance.

**Table 1. Available physical-chemical, environmental fate, ecotoxicity, and mammalian toxicity data for HFE-356mmz1**

<b>PYSICOCHEMICAL PROPERTIES:</b>			
Molecular Weight	182.07	Water Solubility (mg/L) @ 25 °C	1400
Physical State at Room Temp.:	Liquid	Flash Point (°C)	No flash point detected
Melting Point (°C)	-120.25	Partition Coefficient (log K <sub>ow</sub> )	1.81
Boiling Point (°C)	50.95	Auto flammability (°C)	Data waived
Specific Gravity	1.38	Viscosity (mPa s)	No data
Vapor Pressure kPa @ 20 °C	36.05		
<b>ENVIRONMENTAL FATE:</b>			
Biodegradation	Not readily biodegradable		
<b>ECOTOXICITY (FRESHWATER):</b>			
48 hr LC50 ( <i>Daphnia magna</i> )	>100 mg/L (nominal)		
72 hr EC50 ( <i>Pseudokirchneriella subcapitata</i> )	>129.8 mg/L (measured)		
<b>MAMMALIAN TOXICITY:</b>			
Acute oral (rat), mg/kg-bw	>5,000	Reproductive toxicity	No data <sup>1</sup>
Acute inhalation (rat), 4hr, ppm	>28,685	Sensitization	Not a skin sensitizer
Acute dermal (rabbit), mg/kg-bw (LD <sub>50</sub> )	>5000	Skin irritation / corrosion	Slightly irritating
Genetic toxicity	No data <sup>1</sup>	Eye irritation / corrosion	Practically non-irritating
Carcinogenicity	No data <sup>1</sup>		

<sup>1</sup> Not expected based on closely related compounds and relevant exposures during use in vapor cleaning equipment.

HFE-356mmz1 is on the TSCA Inventory following submittal of Premanufacture Notice (PMN) in 2018. In addition, a SNAP Information Notice has been submitted under the Significant New Alternatives Policy program but is still under agency review.

Please contact me if you have any questions about this request or need further clarification.

Kind Regards,



Carl Walther  
Director, Engineered Fluids Technology  
Halocarbon Products Corporation

Via Federal Express with attachments.

**ESTIMATION OF THE GROUND-LEVEL  
ATMOSPHERIC OZONE FORMATION POTENTIAL OF  
1,1,1,3,3,3-HEXAFLUORO-2-METHOXYPROPANE**

Report to  
Halocarbon Products Corporation  
August 26, 2020

By

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**Summary**

Estimates of ground-level atmospheric ozone impacts in the MIR and other ozone reactivity scales have been derived for 1,1,1,3,3,3-hexafluoro-2-methoxypropane (HFMOP or HFE-356mmz1). The ozone impacts were calculated using the SAPRC-11 atmospheric chemical mechanism, with the estimated alternative mechanisms for this compound added. The atmospheric oxidation mechanism of HFMOP has some uncertainties, so both a best estimate and an upper limit reactivity mechanism were derived for this compound. These predicted that the ozone impact of this compound in the MIR scale are 0.026 and 0.034 gm O<sub>3</sub>/gm VOC, for the best estimate and upper limit mechanisms, respectively. These can be compared with the MIR of 0.29 gm O<sub>3</sub>/gm VOC for ethane. These results indicate that the mass-based ozone impact of HFMOP are at least 8 times less than that of ethane, and the molar impacts are lower as well. Therefore, we conclude that HFMOP has a lower ozone impact than ethane regardless of how the ozone impacts are quantified.

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## Introduction

Ozone in photochemical smog is formed from the gas-phase reactions of volatile organic compounds (VOCs) and oxides of nitrogen ( $\text{NO}_x$ ) in sunlight, and control of both VOCs and  $\text{NO}_x$  is required to attain air quality standards for ozone. Many different types of VOCs are emitted into the atmosphere, each reacting at different rates and having different mechanisms for their reactions. Because of this, they can differ significantly in their effects on ozone formation, or their “reactivity”. In recognition of this, the U.S. EPA has exempted certain volatile organic compounds with ozone impacts expected to be less than ethane from regulations as VOC ozone precursors (Dimitriadis, 1999; RRWG, 1999a, EPA 2005), and the California Air Resources Board (CARB) has adopted regulations with reactivity-based adjustments for several types of VOC sources (CARB 1993, 2000) and is investigating their use for other sources (CARB, 2008).

Use of reactivity-based regulations for VOCs require some means to quantify their ozone impacts. The approach that is generally adopted is to use the “incremental reactivity” of the VOC, which is the change in ozone caused by adding a small amount of the VOC to the emissions in an ozone pollution episode, divided by the amount of VOC added (Carter, 1994a; Dimitriadis, 1999; RRWG 1999a,b). It is important to recognize that incremental reactivities depend on both the VOC and the episode where it is emitted, and for atmospheric conditions they must be calculated using computer airshed models using models for the airshed conditions and chemical mechanisms for the atmospheric reactions involved in ground-level ozone formation (Carter, 1994a; RRWG, 1999b). Different ozone reactivity scales can be developed to represent different types of environmental conditions, ozone quantification methods, or models for airshed conditions (Carter, 1994a, RRWG 1999b; Carter et al, 2003), but the most widely used scale is the Maximum Incremental Reactivity (MIR) scale of Carter (1994a). This scale, which has undergone a number of updates using updated chemical mechanisms (Carter, 2000, 2010a-c), is used in the CARB’s current reactivity-based regulations. Ozone impacts in other scales can also be considered when determining reactivity relative to ethane when the EPA makes VOC exemption decisions.

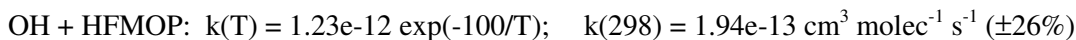
1,1,1,3,3,3-Hexafluoro-2-methoxypropane (HFMOP or HFE-356mmz1) is a compound of interest to the Halocarbon Products Corporation. Its use and manufacture may result in it being emitted into the atmosphere, where it may be subject to VOC regulations aimed at reducing ozone formation. At present there are no published estimates of ozone impacts for this compound, though there are data concerning its atmospheric reaction rates (McGillen et al, 2020). Quantitative atmospheric reactivity estimates are needed to determine whether this is an appropriate candidate for exemption as negligibly reactive under current EPA standards, and to determine what MIR value should be used for it if it were subject to reactivity-based regulations such as those used in California.

In this report we discuss a derivation of the most likely atmospheric reaction mechanisms for HFMOP, which are then used to derive the range of reactivity values in the MIR and other ozone reactivity scales. These results are then compared with reactivity results already derived for ethane and the total mixture of anthropogenic VOC emissions.

## Methods

### Atmospheric Reactions of 1,1,1,3,3,3-Hexafluoro-2-methoxypropane

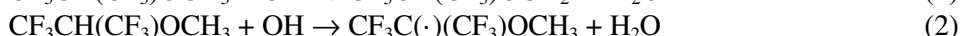
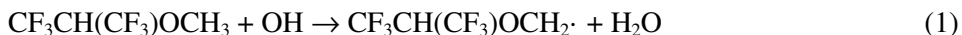
Saturated halogenated ethers such as HFMOP (and most other saturated compounds as well) are expected to react in the atmosphere primarily with OH radicals, although they will also react to some extent with chlorine atoms in some environments. The rate constants for both of these reactions have been measured, and the available kinetic data are summarized and reviewed by McGillen et al (2020), who recommend use of the following rate constant expressions:



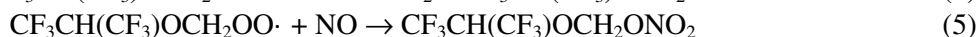
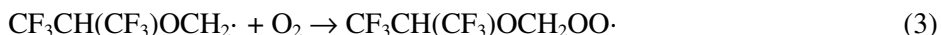
However, the scenarios used to calculate MIR and other reactivity scales are based on environments where chlorine reactions are not important, so we only need to consider the reaction with OH.

Note that the OH radical rate constant for ethane at 298K is  $(2.5 \pm 0.2)\text{e-}13 \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$  (McGillen et al, 2020) which makes HFMOP about 20% less reactive than ethane by this metric, though they overlap within the error limits given by McGillen et al (2020). However, the OH rate constant metric does not take into account effects of the VOC's reaction mechanisms that can also significantly affect ozone impacts, and also the effects of its molecular weight, which cause decreased ozone impacts from given masses of emissions as the molecular weight increases. Therefore, it is necessary to compare the mass-based incremental reactivity of the compounds, so all these factors are taken into account. That requires estimating the mechanisms of the subsequent reactions of the radicals formed in the OH reactions, and the effects of the reactivities of the products that can be formed.

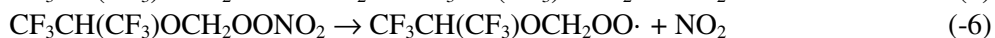
There are two ways OH can react with HFMOP, both involving abstractions of H atoms forming H<sub>2</sub>O and carbon-centered radicals:



Based on structure-reactivity relationships derived from the measured rate constants for the reactions of OH radicals with a wide range of compounds (Vereecken et al, 2018) as implemented in the SAPRC-18 mechanism generation system (Carter, 2019, 2020), we estimate that  $k_1 \gg k_2$ , so we need consider the subsequent reactions of the  $\text{CF}_3\text{CH}(\text{CF}_3)\text{OCH}_2\cdot$  radical. Its primary fate is expected to be first reaction with O<sub>2</sub> forming a peroxy radical, which then reacts primarily with NO to form either the corresponding alkoxy radical or an alkyl nitrate.

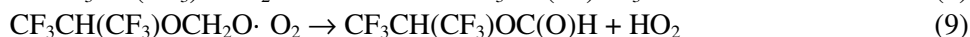
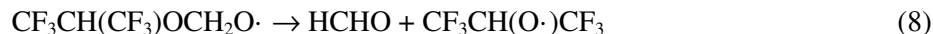


The peroxy radical can also react with NO<sub>2</sub> forming the corresponding peroxy nitrate, but the peroxy nitrate formed is expected to rapidly decompose back to its reactants, resulting in no net reaction.

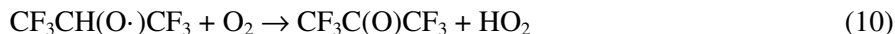


The alkoxy radical formed in Reaction (4) has three possible modes of reaction, as follows:





Since H· atoms are converted to HO<sub>2</sub> in the atmosphere, the overall products formed from Reactions (7) and (9) are the same, namely hexafluoro isopropyl formate and HO<sub>2</sub>. The CF<sub>3</sub>CH(O·)CF<sub>3</sub> product from Reaction (8) is expected to react primarily with O<sub>2</sub>.



Therefore, the overall products formed from Reaction (8) are formaldehyde and perfluoroacetone + HO<sub>2</sub>.

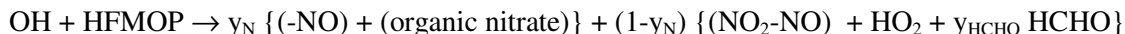
Both hexafluoro isopropyl formate and perfluoroacetone are expected to react relatively slowly in the atmosphere, so their subsequent reactions are expected to have negligible effects on the ozone impact of HFMOP in the one-day scenarios used to calculate the reactivity scales in this work (see below). Therefore, they can either be represented by an inert model species if their calculated atmospheric concentration is of interest, or their formation can be ignored if not. Since the calculations in this work are concerned only about ozone impacts, their formation is not tracked in the model calculations in this work.

When NO<sub>x</sub> is low, peroxy radicals can also react with HO<sub>2</sub> and other peroxy radicals. Reactions with HO<sub>2</sub>, forming a hydroperoxide



are the most important of these processes for most peroxy radicals under atmospheric conditions. However, these reactions only become important when NO<sub>x</sub> is sufficiently low that O<sub>3</sub> formation is NO<sub>x</sub> limited, and neglecting them does not significantly affect O<sub>3</sub> or ozone reactivity predictions, at least in single-day scenarios, and definitely not under relatively high NO<sub>x</sub> MIR conditions (see discussion of MIR calculations below). Nevertheless, these reactions are represented in the model, though in an approximate manner.

If the reactions of peroxy radicals with NO<sub>2</sub> are ignored because they are rapidly reversed and their reactions with HO<sub>2</sub> or other peroxy radicals are ignored because they are not important under conditions where VOCs affect ozone formation, we need to consider only Reactions 1, 3-5 and 7-10 when deriving a model for HFMOP reactions. Based on these, the overall process of the reactions of HFMOP with OH radicals can be given as follows, where (-NO) refers to the consumption of NO in the overall reactions, (NO<sub>2</sub>-NO) is the conversion of NO to NO<sub>2</sub>:



Here, y<sub>N</sub> is the organic nitrate yield in the reactions of the peroxy radical [k<sub>5</sub>/(k<sub>4</sub>+k<sub>5</sub>)], and y<sub>HCHO</sub> is the fraction of the alkoxy intermediate that decomposes to form formaldehyde [k<sub>8</sub>/(k<sub>7</sub>+k<sub>8</sub>+k<sub>9</sub>)]. Note that low reactivity products are not shown because the effects of their formation are assumed to be unimportant.

The values assumed for y<sub>N</sub> and y<sub>HCHO</sub> will affect the reactivity results. Therefore, for the purpose of this project, we will derive two mechanisms: (1) a "best estimate" mechanism using our estimates of the most likely values of these parameters, and (2) a "most reactive" mechanism that uses the values of these parameters that give the greatest ozone impact. These would yield respectively our best estimate and our upper limit estimate for the calculated reactivity values for this compound. The best estimate reactivity values are useful for assessing relative ozone impacts from different VOC sources, while the upper limit values are more appropriate when making VOC exemption decisions

The nitrate formation reaction represents both a radical and NO<sub>x</sub> sink in the overall reactions, which tend to inhibit ozone formation. Therefore, the predicted reactivity of HFMOP would be the highest if it is low, so y<sub>N</sub>=0 is assumed in our "most reactive" mechanism. Nitrate yields have been measured for a number of peroxy radicals and generally range from near zero for smaller radicals such as methyl or ethyl, up to ~30% or higher for very large radicals (e.g., Arey et al, 2001; Yeh and Ziemann, 2014). The effects of halogen substitution on the nitrate yields are unknown, and we are not aware of directly measured nitrate yields from such highly fluorinated radicals. However, overall nitrate yields have been derived from environmental chamber experiments with various halopropenes, and the results are summarized on

Table 1. These are used, along with current general nitrate yield estimation methods, to derive y<sub>N</sub>=0.034 as our best estimate overall nitrate yield for HFMOP.

Table 1. Best fit or estimated overall nitrate yields in the atmospheric reactions of various halopropenes that have been studied.

Starting Compound	Atoms	Y <sub>Nitrate</sub>		Ref
		Est'd [a]	Used	
Trans 1,3,3,3-tetrafluoropropene	C <sub>3</sub> H <sub>2</sub> O <sub>3</sub> F <sub>4</sub>	1.9%	5% [b]	Carter (2009a)
2,3,3,3-Tetrafluoropropene	C <sub>3</sub> H <sub>2</sub> O <sub>3</sub> F <sub>4</sub>	1.9%	~0% [b]	Carter (2009b)
Trans 1-chloro-3,3,3-trifluoropropene	C <sub>3</sub> H <sub>2</sub> O <sub>3</sub> F <sub>3</sub> Cl	1.9%	2.5% [b]	Carter (2009c)
1,1,1,3,3,3-hexafluoro-2-methoxypropane	C <sub>4</sub> H <sub>3</sub> O <sub>3</sub> F <sub>6</sub>	2.6%	3.4% [c]	This work

[a] Estimated using the SAPRC mechanism generation system using parameters derived to fit measured nitrate yields and also nitrate yields that fit results of environmental chamber data.

[b] These are the values used as the best estimate nitrate yields in when estimating ozone impacts of these compounds, based on results of modeling environmental chamber data.

[c] Best estimate mechanism only; yield of 0 used for upper limit mechanism. Derived from the estimated yield multiplied by a correction factor of 2.5%/1.9% based on the data for the C<sub>3</sub> compounds, where 2.5% is taken as representative of the yields derived from the data.

### Chemical Mechanism Used

The chemical mechanism used to derive the reactivity scales used in the current CARB reactivity based regulations (Carter, 2010c) is the SAPRC-07 mechanism of Carter (2010a,b), but the SAPRC-11 mechanism of Carter and Heo (2012, 2013) is used in this work. This is because it is an updated mechanism with improved aromatics chemistry, but still gives essentially the same reactivity predictions for non-aromatic compounds (Carter and Heo, 2012). In fact, SAPRC-07 was used for some initial HFMOP reactivity calculations, but the results were essentially the same as using SAPRC-11. These mechanisms have already been comprehensively documented, so they are not discussed in detail here. The documentation and reactivity scales derived using SAPRC-07 are available online at <http://www.cert.ucr.edu/~carter/SAPRC>.

Briefly, the SAPRC-11 mechanism consists of two major components: the "base" mechanism that is used to represent the full set of VOC emissions from all sources, and the specific mechanisms for the individual VOCs whose ozone impacts are being assessed. The compounds whose incremental reactivity are calculated are represented explicitly, while most of the other VOCs that are emitted into the ozone scenario being modeled are represented using lumped model species in the base mechanism. See Carter

(2010a,b) for a more complete discussion of how the SAPRC-07 is used to represent the various VOCs in reactivity assessment calculations. This discussion is also applicable to SAPRC-11 (Carter and Heo, 2012, 2013).

In order to calculate the incremental reactivities from our estimated mechanisms for HFMOP, it is necessary to represent the reactions and products in terms of SAPRC-07/11 model species, as indicated above. As discussed above, we derived two mechanisms, a "best estimate" and a "most reactive" version, and they are given in terms of SAPRC-07/11 model species in

Table 2. Note that the OH rate constant in the "most reactive" mechanism is increased by ~25% to reflect the upper limit of the range uncertainty in this rate constant.

Table 2. Estimated mechanisms for HFMOP in terms of SAPRC-11 model species

Mechanism	kOH [a]	HFMOP + OH Products [b]
Best estimate	1.94e-13	0.034 {RO2XC + zRNO3} + 0.966 {RO2C + xHO2} + yROOH
Most Reactive	2.43e-13	RO2C + xHO2 + xHCHO + yROOH

[a] Rate constant in  $\text{cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ . The best estimate is based on the recommendation of McGillen et al (2010) for 298K, and the most reactive is based on increasing this by 25%, based on the error limit given by McGillen et al (2020) for the 298K rate constant.

[b] List of SAPRC-11 model species used: RO2XC = NO consumption; RO2C = NO conversion to NO<sub>2</sub>; zRNO3 = formation of RNO3 [used to represent CF<sub>3</sub>CH(CF<sub>3</sub>)OCH<sub>2</sub>ONO<sub>2</sub>] after a reaction of peroxy with NO; xHO2 = formation of a HO2 after a reaction of peroxy with NO; xHCHO = formation of a formaldehyde after a reaction of peroxy with NO; and yROOH = formation of ROOH [used to represent CF<sub>3</sub>CH(CF<sub>3</sub>)OCH<sub>2</sub>OOH] after a reaction of peroxy with HO<sub>2</sub>. These represent the net effects of the reactions discussed in the previous section.

## Scenarios and Reactivity Assessment Methods

The methods, scenarios, and reactivity scales that were used in this reactivity scale update are the same as employed previously for the SAPRC-99 and SAPRC-07 scales (Carter, 1994a, Carter 2000, 2010a-c), and those references should be consulted for detail. Briefly, this is based on the methods and scenarios originally developed by Carter (1994a,b), with slight modifications in the averaging methods as described by Carter (2000). These are based on 39 single-day "base case" EKMA box model scenarios (EPA, 1984) derived by the EPA for assessing how various ROG and NO<sub>x</sub> control strategies would affect ozone nonattainment in various areas of the country (Baugues, 1990). The conditions of these scenarios are summarized on Table A-1 in Appendix A. More details concerning the modeling inputs are given by Carter (1994b).

The base case scenarios with the NO<sub>x</sub> inputs as specified by Bauges (1990) were used to derive the "base case" reactivity scales. Because absolute and even relative impacts of VOCs on O<sub>3</sub> formation are highly dependent on NO<sub>x</sub> conditions that are highly variable in the base case scenarios, scenarios with adjusted NO<sub>x</sub> inputs were derived to obtain scales that are more representative of standard conditions of conditions of NO<sub>x</sub> availability. These are as follows:

- The Maximum Incremental Reactivity (MIR) scale is derived from the scenarios where the NO<sub>x</sub> inputs are adjusted to yield highest incremental reactivities of VOCs. This represents relatively high NO<sub>x</sub> conditions where, by definition, O<sub>3</sub> is most sensitive to changes in VOC emissions.



- The Maximum Ozone Incremental Reactivity (MOIR) scale is derived from the scenarios where NO<sub>x</sub> inputs are adjusted to yield highest maximum O<sub>3</sub> concentrations. This represents NO<sub>x</sub> conditions that are most favorable to O<sub>3</sub> formation.
- The Equal Benefits Incremental Reactivity (EBIR) scale is derived from scenarios where NO<sub>x</sub> inputs are adjusted so that the reduction in O<sub>3</sub> caused by reducing base ROG inputs are the same as those caused by changing total NO<sub>x</sub> inputs by the same percentage. This represents the lowest NO<sub>x</sub> conditions where controls of VOCs are at least as effective as controlling NO<sub>x</sub>; since for lower NO<sub>x</sub> levels NO<sub>x</sub> controls are always more effective for reducing O<sub>3</sub>.

Table A-1 in Appendix A gives the NO<sub>x</sub> levels that correspond to these various conditions of NO<sub>x</sub> availability and summarizes other selected inputs that were used to derive the MIR, MOIR, EBIR or base case scales, and gives the maximum ozone yields that were calculated. The incremental reactivities for those scales were averages of the incremental reactivities calculated for the 39 scenarios of the various types.

The incremental reactivity calculations were carried out by adding an amount of test compound such that the estimated amount reacted would be 0.05% the mole carbon of the base ROG input. The incremental reactivities were calculated as the change in final (i.e., maximum) O<sub>3</sub> concentrations in terms of total moles formed, divided by the moles of test compound or mixture added in the calculations. The incremental reactivities are then converted from mole to mass basis by using the molecular weights for O<sub>3</sub> and the test VOCs.

## Results

The incremental reactivities calculated for the two HFMOP mechanisms for the individual city-specific scenarios are given in Table A-2 in Appendix A, which also gives the reactivities for ethane and the mixture used to represent reactive organic gas (ROG) emissions from all sources in the same scales. The averages from these incremental reactivities are summarized in Table 3. Averages of reactivities of the HFMOP mechanisms relative to ethane are also shown. The reactivities for the HFMOP mechanisms in the individual scenarios are also plotted against those of ethane in Figure 1.

The results show that HFMOP is significantly less reactive than ethane in all scenarios examined, regardless of the mechanism assumed or the type of reactivity scenario. The reactivities relative to ethane are somewhat larger in the MIR scale, but even then ethane has about 8 times the ozone impact of HFMOP, on a mass basis, if the most reactive mechanism is assumed. Our best estimate mechanism predicts that ethane is 10 times more reactive.

Although I don't recommend using molar reactivities as a basis for making exemption decisions, it is noteworthy that HFMOP is also less reactive than ethane on a molar basis. The ratio of mass-based to molar reactivities are inversely proportional to the molecular weight of the compound, and since HFMOP, like most other reactive VOC compounds, has a higher molecular weight as ethane, their ratios of mole based reactivities will be higher than mass based ratios by the ratio of their molecular weight relative to ethane. This ratio is close to 6 for HFMOP. The mole-based ratios are also included on Table 3, where it can be seen that even though they are a factor of 6 higher, they still indicate HFMOP has a lower reactivity than ethane by this metric. However, regardless of the mechanism, the mole-based ratios are all greater than 0.8±0.2, which is the ratio of the OH rate constants.

Table 3. Incremental reactivities calculated for HFMOP, ethane, and the base ROG mixture in the MIR, MOIR, EBIR, and base case scales.

Compound or Mixture	Incremental Reactivity (gm O <sub>3</sub> / gm VOC) [a]			
	MIR	MOIR	EBIR	Base
Ambient ROG Mixture [b]	3.9±0.6	1.5±0.3	0.9±0.2	1.21±0.45
Ethane	0.29±0.07	0.20±0.05	0.14±0.04	0.17±0.04
1,1,1,3,3,3-hexafluoro-2-methoxypropane (HFMOP)				
"Best Estimate" mechanism	0.026±0.005	0.011±0.002	0.006±0.002	0.009±0.003
"Most Reactive" mechanism	0.034±0.006	0.015±0.003	0.009±0.002	0.012±0.004
HFMOP / Ethane Reactivity Ratios (mass basis) [b]				
"Best Estimate" mechanism	0.091±0.011	0.059±0.011	0.045±0.010	0.053±0.017
"Most Reactive" mechanism	0.121±0.014	0.080±0.015	0.066±0.013	0.075±0.022
HFMOP / Ethane Reactivity Ratios (mole basis) [b,c] (Note: molar kOH ratio is 0.8±0.2)				
"Best Estimate" mechanism	0.55±0.06	0.36±0.07	0.27±0.06	0.32±0.11
"Most Reactive" mechanism	0.73±0.09	0.48±0.09	0.40±0.08	0.46±0.13

[a] Error limits are (1  $\sigma$ ) standard deviations of averages over the 39 scenarios of this type and do not reflect mechanism or scenario uncertainties.

[b] Averages of ratios of HCFO/Ethane reactivities for each individual scenarios.

[c] Ratios of reactivities in units of moles O<sub>3</sub> / mole VOC.

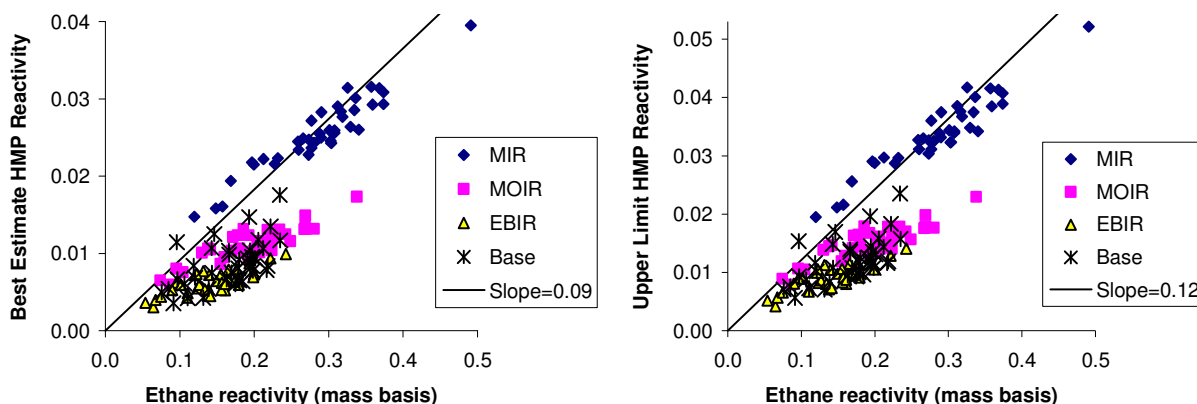


Figure 1. Plots of incremental reactivities of the HFMOP mechanisms relative to ethane for the individual scenarios against the incremental reactivity of ethane .

## Discussion and Conclusions

The ozone impacts of 1,1,1,3,3,3-hexafluoro-2-methoxypropane (HFMOP) are predicted to be less than 4% that of ethane on a mass basis and less than 20% on a molar basis than that of ethane, the compound that has been used as the informal standard to establish negligible ozone impacts for regulatory applications (Dimitriades, 1999). HFMOP is also less reactive than ethane on a molar basis and also on the basis of OH radical rate constants, though the relative reactivities are somewhat higher by the molar metrics. The use of ethane for this purpose is somewhat arbitrary, being more a result of history than of a reasoned analysis of where the optimum cutoff should be from a policy and air quality improvement perspective (RRWG, 1999; Dimitriades 1999). Nevertheless, the ethane standard provides a reasonable input for exemption decisions for compounds that can be shown to have either much greater or much lower ozone impacts than ethane under all conditions.

Note that some have proposed using molar reactivities as a basis of exemption decisions because they are more closely related to fundamental chemistry, though others believe that using mass-based reactivities is more appropriate because VOC emissions are quantified by mass and gives a better approximation of effects of real-world VOC replacements. However, HFMOP also has lower reactivity than ethane by this metric, so this issue does not affect conclusions about reactivity relative to ethane.

The OH radical rate constant is also used as an approximate metric of reactivity, which is appropriate when making exemption decisions for extremely slowly reacting saturated compounds that do not photolyze or react significantly with other atmospheric species. There is an upper limit of how much O<sub>3</sub> can be formed from reactions of a given amount of VOC, so if the rate constant is sufficiently low the compound would be less reactive than ethane regardless of its mechanism. In the case of HFMOP, the OH radical rate constant is slightly less than that for ethane, but they overlap within their uncertainty limits. Therefore, although HFMOP also has a slightly lower reactivity than ethane by the OH rate constant metric, it is not lower by a sufficient amount to be appropriate for exemption without considering other factors. However, the other factors, particularly the molecular weight, indicate a much lower reactivity on a mass basis.

Although the atmospheric reaction mechanism of HFMOP has some uncertainties, even the most reactive reasonable mechanism supports the conclusion that HFMOP is less reactive than ethane. It is clear that this compound meets the ethane reactivity standard, assuming that the estimates and measured OH rate constants are not significantly in error. Ideally the ability of the estimated mechanisms to predict ozone impacts under atmospheric conditions should be tested by determining whether the estimated mechanisms can predict ozone formation observed in environmental chamber experiments, but experimental and modeling studies for similar compounds tend to support the mechanism estimation methods used in this work. Therefore it is considered to be unlikely that these relative reactivity estimates in this work are significantly in error.

## Disclaimer

The opinions and conclusions in this report are entirely those of the author.

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## **Appendix A. Detailed Scenario Results**

Table A-1 give selected input conditions for the various scenarios used for reactivity assessment, and calculated incremental reactivities for the mixture used in the calculations to represent VOC emissions from all anthropogenic sources. Table A-2 gives the incremental reactivity results for ethane and the two HFMOP mechanisms discussed in the text.

Table A-1. Scenarios used for reactivity assessment, with selected inputs, calculated maximum ozone concentrations, and incremental reactivities of the base ROG mixture used to represent anthropogenic emissions from all sources.

Scenario	Max Height (km)	O3 Aloft (ppb)	ROG Input [a]	NOx Input [a]				Maximum O3 (ppb)				Incremental Reactivities of base ROG (mass basis)			
				Base	MIR	MOIR	EBIR	Base	MIR	MOIR	EBIR	Base	MIR	MOIR	EBIR
Average	1.8	70	15.4	2.34	4.23	2.79	1.78	231	190	245	229	1.21	3.94	1.55	0.87
St.Dev	0.7	17	8.3	1.27	1.65	1.13	0.69	83	63	90	84	0.45	0.62	0.29	0.21
Atlanta, GA	2.1	63	11.8	1.62	3.40	2.26	1.58	175	148	183	174	0.96	3.67	1.59	0.92
Austin, TX	2.1	85	11.2	1.21	3.47	2.28	1.43	174	147	193	181	0.78	3.85	1.73	0.98
Baltimore, MD	1.2	84	16.8	3.26	4.47	2.92	1.70	329	251	331	301	1.79	4.08	1.49	0.76
Baton Rouge, LA	1.0	62	11.1	1.63	2.67	1.82	1.37	243	192	245	235	0.95	3.19	1.25	0.67
Birmingham, AL	1.8	81	12.8	1.85	4.89	3.25	2.08	243	208	268	250	0.96	4.88	1.88	1.08
Boston, MA	2.6	105	14.3	2.20	5.42	3.55	2.23	194	166	206	195	0.89	3.61	1.49	0.91
Charlotte, NC	3.0	92	7.5	0.96	4.19	2.74	1.97	140	141	167	162	0.65	3.75	1.77	1.27
Chicago, IL	1.4	40	25.0	2.15	6.07	4.08	2.63	291	250	335	311	0.46	3.86	1.31	0.66
Cincinnati, OH	2.8	70	17.3	2.71	5.41	3.53	1.96	200	162	205	187	1.33	4.29	1.78	0.98
Cleveland, OH	1.7	89	15.7	2.37	3.84	2.45	1.60	251	199	251	236	1.38	3.55	1.46	0.78
Dallas, TX	2.3	75	17.5	3.70	4.55	2.98	2.04	203	167	212	201	2.45	3.58	1.46	0.81
Denver, CO	3.4	57	29.3	4.64	6.30	4.14	2.66	204	168	206	193	1.72	3.40	1.36	0.69
Detroit, MI	1.8	68	17.3	2.54	4.91	3.22	1.78	242	188	247	224	1.19	4.13	1.57	0.84
El Paso, TX	2.0	65	12.3	1.86	2.83	1.84	1.31	183	149	183	175	1.55	3.52	1.52	0.82
Hartford, CT	2.3	78	10.7	1.28	4.01	2.58	1.53	169	152	191	177	0.93	4.55	1.91	1.12
Houston, TX	1.7	65	25.5	4.19	6.71	4.45	2.79	312	232	312	288	1.29	4.05	1.44	0.73
Indianapolis, IN	1.7	52	12.1	1.82	3.23	2.01	1.29	210	162	211	197	1.48	4.36	1.66	0.92
Jacksonville, FL	1.5	40	7.7	1.01	2.29	1.54	1.10	152	129	163	156	0.80	3.98	1.57	0.91
Kansas City, MO	2.2	65	9.1	1.28	3.14	2.03	1.10	154	130	164	149	1.23	4.60	1.93	1.10
Lake Charles, LA	0.5	40	7.0	0.94	2.09	1.45	1.04	293	237	319	302	0.57	4.25	1.32	0.70
Los Angeles, CA	0.5	100	23.1	3.04	4.69	3.12	2.14	587	418	588	552	0.81	2.69	0.87	0.43
Louisville, KY	2.5	75	13.7	2.48	4.55	2.93	1.96	208	167	211	199	1.47	4.48	1.89	1.09
Memphis, TN	1.8	58	14.9	2.20	4.83	3.22	2.01	228	182	240	223	0.98	4.68	1.62	0.88
Miami, FL	2.7	57	9.5	0.98	3.59	2.32	1.58	130	125	154	147	0.60	4.21	1.76	1.10
Nashville, TN	1.6	50	7.4	0.92	3.07	2.03	1.29	164	150	194	181	0.83	5.55	2.14	1.25
New York, NY	1.5	103	39.2	4.85	8.86	6.38	4.25	378	311	391	367	0.59	2.96	0.96	0.48
Philadelphia, PA	1.8	53	19.0	3.07	4.96	3.29	2.06	243	185	243	226	1.29	4.06	1.43	0.75
Phoenix, AZ	3.3	60	39.9	5.26	8.53	5.50	3.13	281	217	281	253	1.58	4.09	1.70	0.81
Portland, OR	1.6	66	6.2	0.96	2.21	1.37	0.95	162	133	169	162	1.12	4.24	1.81	1.11
Richmond, VA	1.9	64	16.4	2.65	4.90	3.22	1.79	237	185	241	219	1.29	4.29	1.64	0.88
Sacramento, CA	1.1	60	7.4	1.12	2.04	1.33	0.85	202	159	205	191	1.37	4.56	1.77	0.97
St Louis, MO	1.6	82	25.6	4.22	5.85	3.85	2.26	323	245	324	297	1.55	3.63	1.29	0.65
Salt Lake City, UT	2.2	85	10.7	1.26	3.27	2.08	1.21	184	161	196	182	1.09	4.15	1.90	1.06
San Antonio, TX	2.3	60	6.0	1.53	2.17	1.39	1.00	126	105	127	123	1.94	3.56	1.66	1.07
San Diego, CA	0.9	90	7.7	1.08	1.75	1.16	0.82	192	153	193	184	0.95	2.76	1.10	0.60
San Francisco, CA	0.7	70	25.0	5.24	4.36	2.97	2.19	261	362	477	454	2.10	2.38	0.86	0.42
Tampa, FL	1.0	68	7.9	1.81	2.44	1.66	1.21	226	181	227	218	1.80	3.89	1.45	0.83
Tulsa, OK	1.8	70	14.9	2.80	4.64	3.02	1.77	226	176	226	208	1.42	4.29	1.59	0.86
Washington, DC	1.4	99	13.5	2.54	4.53	3.03	1.89	280	218	284	264	1.20	4.15	1.53	0.87

Table A-2. Incremental reactivity results for ethane and the two mechanisms for 1,1,1,3,3,3-hexafluoro-2-methoxypropane (HFMOP).

Scenario	Incremental Reactivities (mass basis)											
	Ethane				HFMOP: Most Reactive Mechanism				HFMOP: Best estimate mechanism			
	Base	MIR	MOIR	EBIR	Base	MIR	MOIR	EBIR	Base	MIR	MOIR	EBIR
Average	0.17	0.29	0.20	0.14	0.012	0.034	0.015	0.009	0.009	0.026	0.011	0.006
St.Dev	0.04	0.07	0.06	0.04	0.004	0.006	0.003	0.002	0.003	0.005	0.002	0.002
Atlanta, GA	0.14	0.27	0.19	0.14	0.011	0.033	0.017	0.010	0.008	0.025	0.012	0.007
Austin, TX	0.14	0.28	0.23	0.16	0.008	0.031	0.017	0.010	0.005	0.024	0.012	0.007
Baltimore, MD	0.21	0.27	0.19	0.14	0.016	0.033	0.013	0.007	0.012	0.025	0.010	0.005
Baton Rouge, LA	0.12	0.21	0.14	0.10	0.012	0.030	0.014	0.009	0.008	0.022	0.011	0.006
Birmingham, AL	0.18	0.37	0.27	0.20	0.010	0.041	0.018	0.011	0.006	0.031	0.013	0.007
Boston, MA	0.16	0.30	0.22	0.17	0.009	0.032	0.015	0.010	0.007	0.025	0.011	0.007
Charlotte, NC	0.13	0.34	0.27	0.22	0.007	0.034	0.018	0.013	0.004	0.026	0.013	0.009
Chicago, IL	0.09	0.26	0.16	0.11	0.006	0.033	0.013	0.007	0.004	0.024	0.010	0.005
Cincinnati, OH	0.22	0.33	0.25	0.18	0.012	0.035	0.016	0.009	0.008	0.026	0.012	0.006
Cleveland, OH	0.17	0.23	0.17	0.12	0.014	0.030	0.014	0.008	0.010	0.022	0.010	0.005
Dallas, TX	0.23	0.26	0.18	0.13	0.024	0.031	0.015	0.009	0.018	0.023	0.011	0.006
Denver, CO	0.15	0.20	0.13	0.09	0.017	0.029	0.014	0.008	0.013	0.022	0.010	0.005
Detroit, MI	0.20	0.30	0.22	0.16	0.011	0.032	0.014	0.008	0.008	0.024	0.010	0.005
El Paso, TX	0.14	0.20	0.14	0.10	0.015	0.029	0.015	0.009	0.011	0.022	0.011	0.006
Hartford, CT	0.18	0.36	0.27	0.20	0.009	0.038	0.018	0.011	0.006	0.029	0.013	0.007
Houston, TX	0.19	0.30	0.20	0.14	0.013	0.034	0.014	0.008	0.009	0.026	0.010	0.005
Indianapolis, IN	0.19	0.31	0.21	0.15	0.015	0.039	0.016	0.010	0.010	0.029	0.012	0.006
Jacksonville, FL	0.12	0.29	0.19	0.13	0.010	0.037	0.018	0.011	0.007	0.028	0.013	0.008
Kansas City, MO	0.22	0.37	0.28	0.20	0.012	0.039	0.018	0.011	0.008	0.029	0.013	0.007
Lake Charles, LA	0.11	0.33	0.18	0.12	0.009	0.042	0.016	0.010	0.006	0.031	0.012	0.007
Los Angeles, CA	0.09	0.15	0.09	0.07	0.008	0.021	0.008	0.004	0.005	0.016	0.006	0.003
Louisville, KY	0.24	0.37	0.27	0.19	0.016	0.041	0.020	0.012	0.012	0.031	0.015	0.009
Memphis, TN	0.17	0.36	0.23	0.16	0.011	0.042	0.017	0.010	0.008	0.032	0.013	0.007
Miami, FL	0.11	0.32	0.22	0.17	0.007	0.038	0.018	0.012	0.004	0.028	0.013	0.008
Nashville, TN	0.18	0.49	0.34	0.24	0.010	0.052	0.023	0.014	0.007	0.040	0.017	0.010
New York, NY	0.08	0.17	0.10	0.07	0.007	0.026	0.011	0.006	0.005	0.019	0.008	0.004
Philadelphia, PA	0.18	0.29	0.19	0.13	0.013	0.034	0.014	0.008	0.009	0.026	0.010	0.005
Phoenix, AZ	0.20	0.28	0.21	0.14	0.013	0.033	0.014	0.007	0.009	0.024	0.010	0.005
Portland, OR	0.18	0.32	0.23	0.18	0.012	0.037	0.018	0.012	0.008	0.028	0.013	0.008
Richmond, VA	0.20	0.29	0.22	0.16	0.012	0.033	0.015	0.008	0.008	0.025	0.011	0.005
Sacramento, CA	0.20	0.34	0.23	0.16	0.014	0.040	0.017	0.010	0.010	0.030	0.012	0.007
St Louis, MO	0.17	0.23	0.16	0.11	0.014	0.029	0.012	0.007	0.010	0.022	0.009	0.004
Salt Lake City, UT	0.18	0.31	0.24	0.17	0.010	0.034	0.017	0.010	0.007	0.026	0.012	0.006
San Antonio, TX	0.22	0.27	0.20	0.16	0.018	0.030	0.016	0.011	0.013	0.023	0.012	0.007
San Diego, CA	0.10	0.16	0.10	0.08	0.009	0.022	0.010	0.007	0.007	0.016	0.008	0.004
San Francisco, CA	0.10	0.12	0.07	0.05	0.015	0.020	0.009	0.005	0.011	0.015	0.007	0.004
Tampa, FL	0.19	0.28	0.17	0.12	0.020	0.036	0.016	0.011	0.015	0.027	0.012	0.007
Tulsa, OK	0.21	0.33	0.22	0.16	0.014	0.037	0.016	0.009	0.011	0.029	0.012	0.006
Washington, DC	0.19	0.31	0.22	0.16	0.012	0.034	0.014	0.009	0.008	0.026	0.011	0.006